

## CLAIMS

1. A multilayer pipe having an inner layer of a thermoplastic polymer and a contoured, metallic barrier layer deposited thereon.  
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2. A multilayer pipe having a stabilised inner layer of a thermoplastic polymer and a contoured, metallic barrier layer deposited thereon, wherein the inner layer comprises an extruded thermoplastic polymer comprising at least one polar stabilizer, wherein:  
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  - (i) the thermoplastic polymer is provided with pendant polar functional groups, and/or
  - (ii) the thermoplastic polymer comprises an effective amount of at least one filler provided with pendant polar functional groups, and/or  
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  - (iii) The thermoplastic polymer comprises a blend of a non-polar thermoplastic polymer and a thermoplastic polymer provided with pendant polar functional groups.
3. A multilayer pipe according to claim 1 or 2, wherein the contoured metallic barrier layer is disposed between the thermoplastic polymer inner layer and one or more additional outer layers.  
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4. A multilayer pipe according to any one of the preceding claims, wherein the thermoplastic polymer of the inner layer comprises a polyolefin.  
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5. A multilayer pipe according to claim 4, wherein the polyolefin is polyethylene or polypropylene.

6. A multilayer pipe according to claim 4, wherein the polyolefin is cross-linked polyethylene.
7. A multilayer pipe according to any one of the preceding claims, wherein the thermoplastic polymer of  
5 the inner layer comprises a polar functional polyolefin.
8. A multilayer pipe according to any one of the preceding claims, wherein the thermoplastic polymer of the inner layer comprises a polar functional polyolefin produced by grafting of polar functional groups or  
10 monomers onto a polyolefin backbone.
9. A multilayer pipe according to claim 8, wherein the polar functional polyolefin polymer is a polar functional polyethylene.
10. A multilayer pipe according to any of claims 7 to 9,  
15 wherein the polar functional polyethylene is ethylene/glycidyl methacrylate.
11. A multilayer pipe according to any one of the preceding claims, wherein the thermoplastic polymer of the inner layer comprises a blend of a non-polar semi-crystalline polyolefin polymer and a polar functional  
20 polyolefin polymer.
12. A multilayer pipe according to claim 11, wherein the thermoplastic polymer comprises a blend of a polyethylene polymer and a polar functional polyethylene polymer.
- 25 13. A multilayer pipe according to claim 12, wherein the blend of polyethylene polymers is cross-linked.

14. A multilayer pipe according to any one of the preceding claims, wherein the outer metallic barrier layer comprises aluminium, stainless steel, or copper.
15. A multilayer pipe according to claim 14, wherein the  
5 metallic layer is sputtered, sprayed, plasma coated, galvanically-coated or electro-deposited.
16. A multilayer pipe according to claim 15, wherein the outer barrier layer is directly bonded to the inner thermoplastic polymer layer.
- 10 17. A multilayer pipe according to any one of the preceding claims, wherein the thickness of the deposited metallic barrier is such that the metallic layer acts as a barrier to limit oxygen and water vapour diffusion into the inner thermoplastic polymer layer and also impedes  
15 diffusion of stabilisers and other additives out from the inner thermoplastic polymer layer.
18. A multilayer pipe according to any one of the preceding claims, wherein the metallic layer is at least 0.01  $\mu\text{m}$ , in thickness.
- 20 19. A multilayer pipe according to claim 18, wherein the metallic layer is from 0.05  $\mu\text{m}$  to 5  $\mu\text{m}$  in thickness.
20. A multilayer pipe according to any one of the preceding claims, wherein the deposited metallic barrier layer and the outer surface of the inner layer are  
25 convoluted, either helically or circumferentially, corrugated, ribbed, or patterned such that their surfaces vary in cross-section along the length of the pipe in a regular fashion.

21. A. multilayer pipe according to claim 20, wherein the contoured surfaces of the deposited metallic barrier layer and the outer surface of the inner layer are formed with sinusoidal corrugations.
- 5 22. A multilayer pipe according to any one of the preceding claims, wherein the inner thermoplastic polymer layer comprises a polymeric matrix provided with functional groups that also increase the wetting of the deposited metallic barrier layer by the polymeric matrix.
- 10 23. A multilayer pipe according to any one of the preceding claims, wherein the surface of the metal barrier layer is modified to improve its wetting behaviour.
24. A multilayer pipe according to any one of claims 2 to 15 23, wherein the polar stabiliser is a phenolic antioxidant, a phosphite, a phosphonite, a benzotriazole, or a sterically-hindered amine.
25. A multilayer pipe according to any one of claims 2 to 24, wherein the stabiliser is present in the inner 20 polymeric layer in an amount of from 0.01 to 5 weight percent, based on the weight of the inner polymeric layer.
26. A multilayer pipe according to any one of claims 2 to 25, wherein the filler is inorganic-based filler.
- 25 27. A multilayer pipe according. to any one of claims 2 to 26, wherein the inorganic-based filler comprises talc, mica, calcium carbonate, kaolin, clay, magnesium hydroxide, calcium silicate, carbon black, graphite, iron

powder, silica, diatomite, titanium oxide, iron oxide, pumice, antimony oxide, dolomite, dawsonite, zeolitic filler, vermiculite, montmorillonite, or hydrated alumina.

- 5 28. A multilayer pipe according to any one of claims 2 to 27, wherein the inorganic-based filler has a mean particle diameter of up to 10  $\mu\text{m}$ .
29. A multilayer pipe according to any one of claims 2 to 28, wherein the inorganic-based filler (s) content of the  
10 inner polymeric layer is from 0.5 to 25 weight percent, based on the weight of the polymeric matrix.
30. A multilayer pipe according to any one of claims 2 to 29, wherein the filler has pendant functional polar groups on its surface, or has been treated to produce  
15 such surface functional groups.
31. A multilayer pipe according to any one of claims 2 to 30, wherein the filler comprises talc or mica.
32. A multilayer pipe according to any one of claims 2 to 31, wherein the filler comprises calcium carbonate.
- 20 33. A multilayer pipe according to any one of claims 2 to 29, wherein the filler comprises hydrated alumina.
34. A multilayer pipe according to any one of claims 2 to 33, wherein the filler is a nanofiller.
35. A multilayer pipe according to claim 34, wherein the  
25 nanofiller is derived from intercalated and exfoliated

clay, a layered silicate, calcium carbonate, calcium phosphate, silicon carbide, or silica.

36. A multilayer pipe according to claim 34 or 35,  
wherein the nanofiller is present in an amount of from 1%  
5 to 5% by volume, based on the volume of the inner  
polymeric layer.

37. A multilayer pipe according to any one of claims 34  
to 36, wherein the particles of the nanofiller are  
substantially uniformly dispersed in the inner polymeric  
10 layer.

38. A multilayer pipe according to any one of claims 34  
to 37, wherein at least 50% of the nanofiller particles  
are less than about 20 layers thick, the layers of the  
nanofiller particles having a unit thickness of from  
15 0.7nm to 1. 2nm.

39. A multilayer pipe according to claim 34, wherein the  
nanofiller is a layered silicate.

40. A multilayer pipe according to claim 39, wherein the  
layered silicate comprises montmorillonite, talc,  
20 magadiite, mica, laponite, or fluorohectorite.

41. A multilayer pipe according to claim 40, wherein the  
layered silicate comprises montmorillonite.

42. A multilayer pipe according to claim 40, wherein the  
layered silicate comprises cloisite.

43. A multilayer pipe according to any one of claims 39 to 42,, wherein the layered silicate nanofiller is provided with functional groups disposed on its surface.
44. A multilayer pipe according to claim 43, wherein the  
5 layered silicate nanofiller has been subjected to an organophilic treatment to give improved thermal stability.
45. A multilayer pipe according to any one of claims 39 to 44, wherein the nanofiller is a layered silicate  
10 comprising particles having one average dimension of 0.002 to 1  $\mu$ m and a thickness of 0.6 to 2.0 nm.
46. A multilayer pipe according to any one of claims 2 to 45, wherein an adhesive layer is disposed between the inner polymeric layer and the contoured deposited  
15 metallic barrier layer.
47. A multilayer pipe according to claim 46, wherein the adhesive layer comprises a polymer comprising one or more functional groups selected from carboxyl, carboxylic, anhydride, epoxy, hydroxyl, isocyanate, aldehyde ester,  
20 acid amide, amino, hydrolysable silyl, or cyano.
48. A multilayer pipe according to any one of the preceding claims, which is provided with an additional outer polymeric layer.
49. A multilayer pipe according to claim 78, wherein the  
25 additional outer polymeric layer comprises cross-linked polyethylene.

50. A multilayer pipe substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

51. A multilayer pipe according to any one of the  
5 preceding claims substantially as hereinbefore described.

52. A method of producing a multilayer pipe comprising an inner layer of a thermoplastic polymer and a metallic barrier layer, which comprises extruding a polymeric composition comprising a thermoplastic polymer to form an  
10 inner layer having a contoured outer surface and depositing a metallic barrier layer onto the contoured surface.

53. A method according to claim 52, wherein the thermoplastic polymer comprises at least one polar  
15 stabilizer, and wherein: (i) the thermoplastic polymer is provided with pendant polar functional groups, and/or (ii) the thermoplastic polymer comprises an effective amount of at least one filler provided with pendant polar functional groups, and/or (iii) The thermoplastic polymer  
20 comprises a blend of a non-polar thermoplastic polymer and a thermoplastic polymer provided with pendant polar functional groups.

54. A method according to claim 53, wherein the inner layer is separately extruded in a first step.



55. A method according to claim 54, wherein the inner layer is extruded using a corrugator.
56. A method according to claim 54, wherein the inner layer is extruded using an extruder provided with a  
5 rotating die to provide a pipe having a smooth inner wall and a helically corrugated outer wall.
57. A method according to any one of claims 54 to 56, wherein an internal mandrel is used to provide increased pressure on the corrugated outer wall and thereby obtain  
10 a smooth contoured outer surface on the inner layer for deposition of the metallic barrier layer.
58. A method according to any one of claims 54 to 57, wherein the metallic barrier layer is deposited on the outer contoured surface of the inner layer to a thickness  
15 suitable to obtain the desired barrier properties against moisture, oxygen and organic contaminants.
59. A method according to any one of claims 54 to 58, wherein the metallic barrier layer is deposited by a sputtering technique.
- 20 60. A method according to any one of claims 54 to 58, wherein the metallic barrier layer is deposited by arc spraying, flame spraying, plasma spraying, or HVOF.
61. A method according to any one of claims 52 to 60, wherein the surface of the metallic barrier layer is  
25 modified to improve its wetting behaviour.

62. A method according to claim 61, wherein the metallic barrier layer is treated by physical surface modification.
63. A method according to claim 62, wherein the metallic  
5 barrier layer is treated by plasma treatment, abrasion, ablation, or cleaning.
64. A method according to claim 61, wherein the metallic barrier layer is treated by chemical surface modification.
- 10 65. A method according to claim 64, wherein the metallic barrier layer is treated by solvent or chemical cleaning, treatment with chemical modifying agents to introduce surface functional groups, deposition of surface layers by plasma deposition of a polymeric layer containing  
15 functional groups, deposition of a glassy layer, or other surface coating techniques.
66. A method according to any one of claims 52 to 65, wherein an additional outer polymeric layer is extrusion coated onto the contoured metallic barrier layer.
- 20 67. A method according to claim 66, wherein the extruded additional outer layer provides a smooth outer surface for the pipe.
68. A method according to any one of claims 52 to 67 substantially as hereinbefore described.
- 25 69. A multilayer pipe according to any one of claims 1 to 51, produced using a method according to any one of claims 52 to 68.

70. A bendable multilayer pipe according to any one of claims 1 to 51 comprising an inner wall, a metallic barrier layer and an outer wall, wherein the compressive E-modulus of the inner layer is lower than the  
5 compressive E-modulus of the outer layer.

71. Use of a multilayer pipe according to any one of claims 1 to 51 in a hot water transport system.

72. A multilayer plastics pipe comprising a plastics inner layer, a metallic barrier layer and a plastics  
10 outer layer, wherein the pipe is capable of axial deformation and the compressive E-modulus of the inner layer is lower than the compressive E-modulus of the outer layer.